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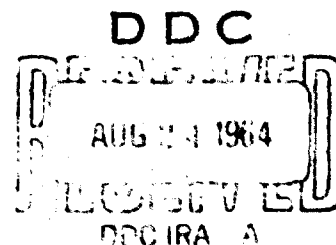
The Infrared Spectra of Perfluorocyclopropane and Cis- and Trans-Perfluorobutene-2

24 JULY 1964

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THE INFRARED SPECTRA OF PERFLUOROCYCLOPROPANE
AND CIS- AND TRANS-PERFLUOROBUTENE-2

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ABSTRACT

The infrared spectra in the NaCl region of cC_3F_6 , $\text{cis-C}_4\text{F}_8$ -2, and $\text{trans-C}_4\text{F}_8$ -2 are reported. Partial vibration assignments are discussed.

THE INFRARED SPECTRA OF PERFLUOROCYCLOPROPANE AND CIS- AND TRANS-PERFLUOROBUTENE-2

We wish to report the infrared spectra in the NaCl region of three simple fluorocarbons. The preparation and purification procedure of the compounds cC_3F_6 , $\text{cis-C}_4\text{F}_8\text{-2}$, and $\text{trans-C}_4\text{F}_8\text{-2}$ is described by Greene and Wachi (Ref. 1). For the cis and trans compounds, it was necessary that we perform the purification procedure twice for complete separation. The spectra were obtained on a Perkin-Elmer 21 infrared spectrometer and are shown in Fig. 1. The bands and their relative intensities are listed in Table I.

The infrared spectrum of cC_3F_6 has not been previously reported. The molecular symmetry is D_{3h} , and the only allowed infrared fundamental vibrations are the two A_2'' and the four E' bands. The two intense bands at 1368 and 1272 cm^{-1} must consist mainly of C-F stretching motions. Thus, one of these is an A_2'' band and the other an E' band. It is not clear which is which. However, there are some indications to suggest that the 1368 cm^{-1} band has A_2'' symmetry and the 1272 cm^{-1} band has E' symmetry. The A_2'' band involves the asymmetric stretching motion of the CF_2 group, whereas the E' band involves the symmetric stretching motion. Usually the asymmetric mode has higher frequency, which corresponds to the assignments of cC_3H_6 (Refs. 2, 3). Furthermore, if the 2532 cm^{-1} band is the overtone of the 1272 cm^{-1} band, then the latter band must be of E' symmetry as the overtones of A_2'' bands are symmetry forbidden. The disturbing feature is that asymmetric bands usually are more intense, but our assignment requires the reverse.

The strong band at 859 cm^{-1} corresponds undoubtedly to the CF_2 deformation of E' symmetry. The two bending frequencies associated with the motion of the CF_2 groups relative to the carbon skeleton lie below 650 cm^{-1} and are not observed. The E' ring deformation frequency of cyclopropyl compounds usually lies within 25 cm^{-1} of 1025 cm^{-1} (Ref. 4). No such band appears in our spectrum; thus, from this point of view, cC_3F_6 must be considered atypical. We tentatively assign the 978 cm^{-1} band to this mode.

The weak band at 2532 cm^{-1} must be either a combination or an overtone of C—F stretching modes. Only seven such possibilities are consistent with the symmetry selection rules: These are the overtones of the E' or E'' bands or the five combinations $\text{A}'_1 \times \text{A}''_2$, $\text{E}' \times \text{A}'_1$, $\text{E}'' \times \text{A}''_2$, $\text{E}' \times \text{E}'$, and $\text{E}' \times \text{E}''$. The overtone of the E' band seems very attractive as 2532 is almost twice 1272, a result that would be expected if anharmonicity were considered.

The infrared spectrum has been reported for mixtures of cis- and trans- C_4F_8 -2 (Refs. 5,6) but not for the pure geometric isomers. If the internal rotations of the CF_3 groups are nearly free, then the trans and cis compounds have C_{2h} and C_{2v} symmetry, respectively. Table II gives the symmetry classes and approximate descriptions of the vibrations.

For the trans molecule, all the gerade vibrations are symmetry forbidden in the infrared spectrum. Thus, there are five stretching modes that should be active. Three of these are surely the intense bands at 1193, 1242, and 1292 cm^{-1} . The band at 882 cm^{-1} also might correspond principally to stretching motions. At least one (and maybe two) of the stretching bands is

•

not readily discernable, it is probably completely or partially obscured by the other bands. All the observed overtone bands must be combinations of gerade and ungerade bands. As a result, the C=C stretch must participate in the overtone bands at 2932 and 3003 cm^{-1} (except in the unlikely event that they are triple combinations). If the intense bands at 1242 and 1292 cm^{-1} are respectively the other participating bands, then the differences are 1711 and 1690 cm^{-1} respectively in reasonably close agreement. Allowing for some anharmonicity sets the C=C stretching frequency at $1710 \pm 20 \text{ cm}^{-1}$, which correlates nicely with the corresponding frequency in the cis molecule.

For cis-C₄F₈-2, all bands are allowed in the infrared spectrum, though some may be weak. The band at 1724 cm^{-1} is the double bond stretch. Of the remaining ten stretching modes, at least five are observed at 1111, 1193, 1224, 1245, and 1350 cm^{-1} . The band at 952 cm^{-1} is also likely to contain considerable stretching motion. The other four stretching motions either are weak bands or are completely or partially obscured.

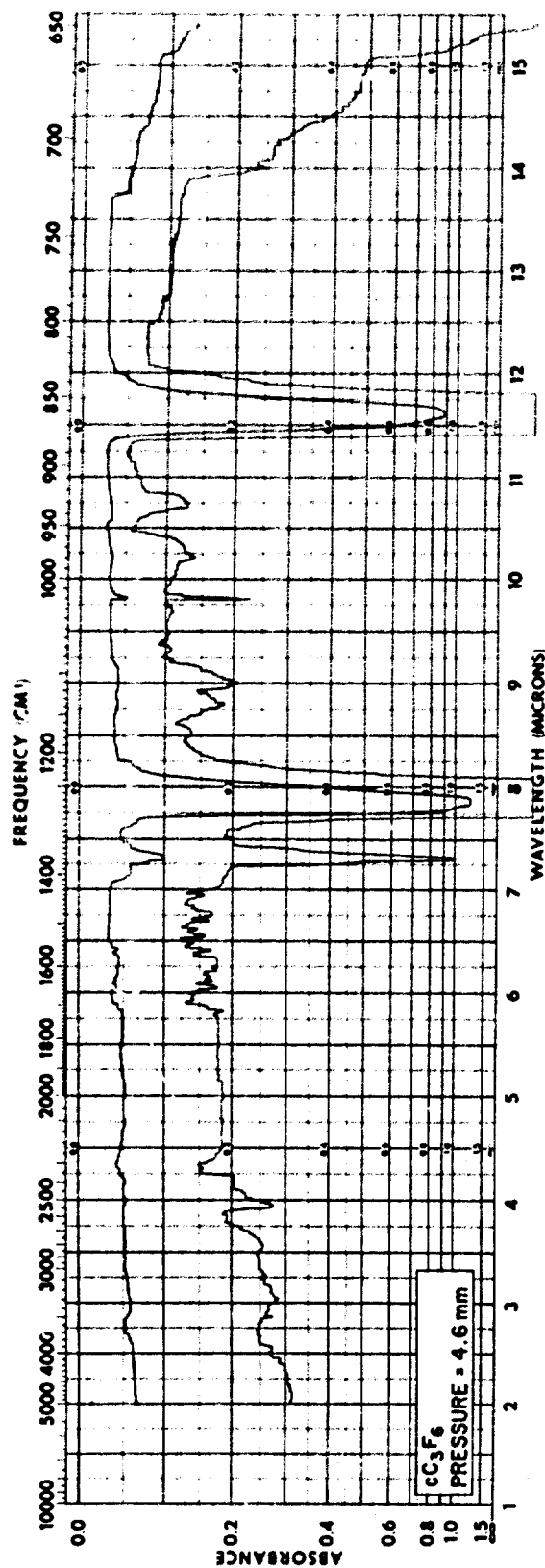


Fig. 1. Infrared spectra.

Path length 10 cm. Discontinuity at 9.82 μ due to change in optical system. For the curve with more intense absorption, the ordinate has been magnified five times.

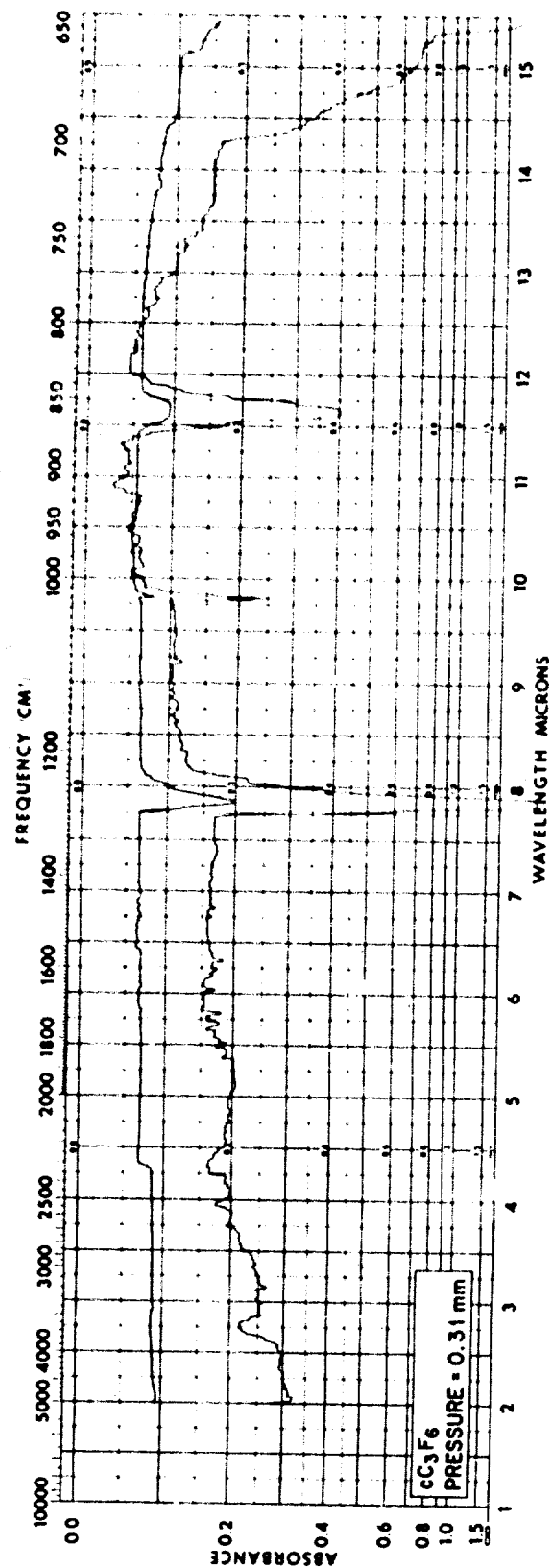


Fig. 1. Infrared spectra. (Continued)

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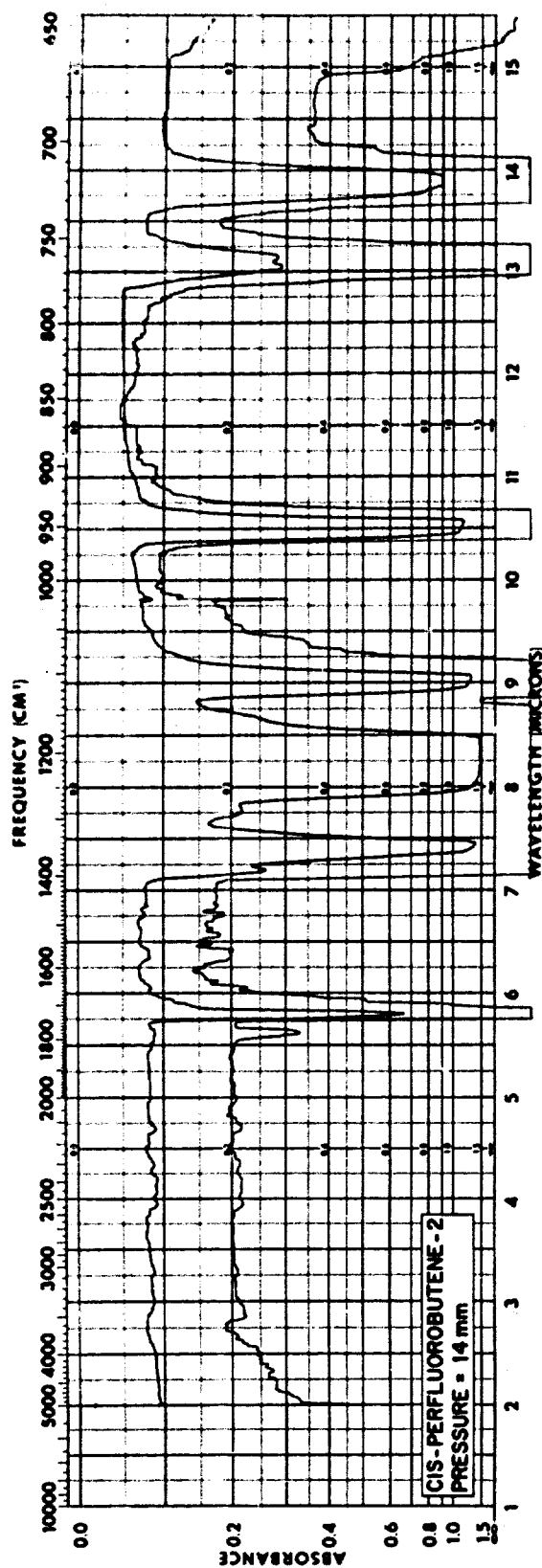


Fig. 1. Infrared spectra. (Continued)

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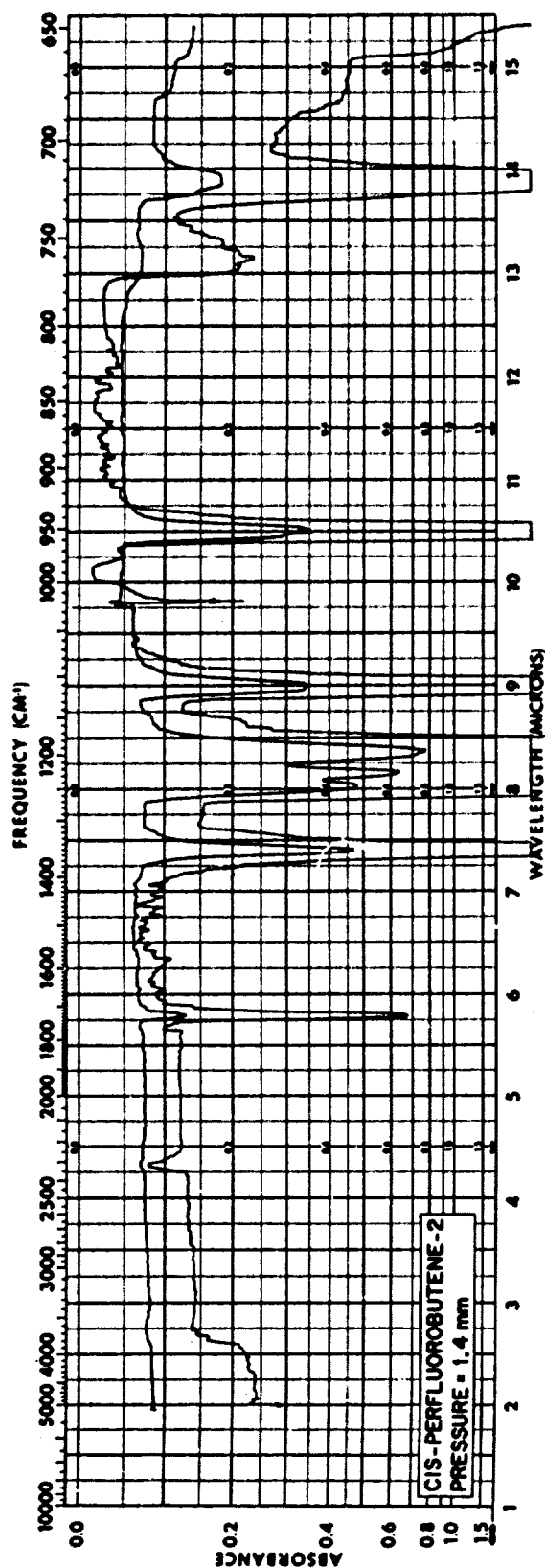


Fig. 1. Infrared spectra. (Continued)

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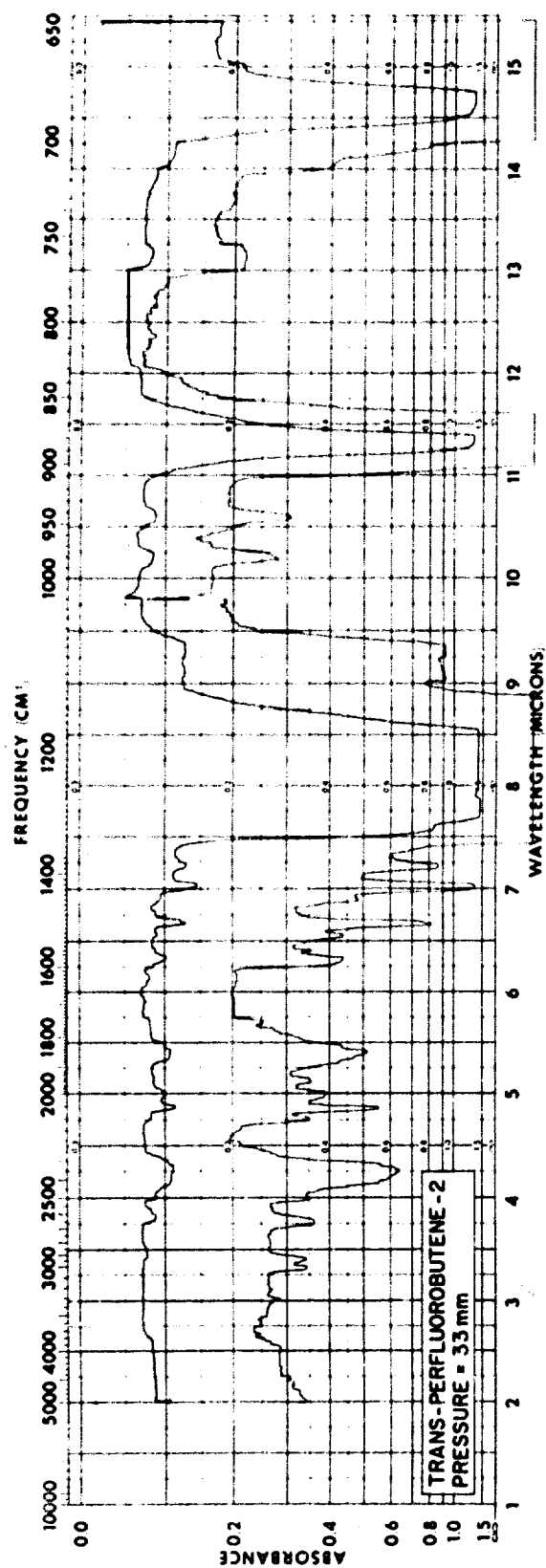


Fig. 1. Infrared spectra. (Continued)

Path length 10 cm. Discontinuity at 9.82 μ due to change in optical system. For the curve with more intense absorption, the ordinate has been magnified five times.

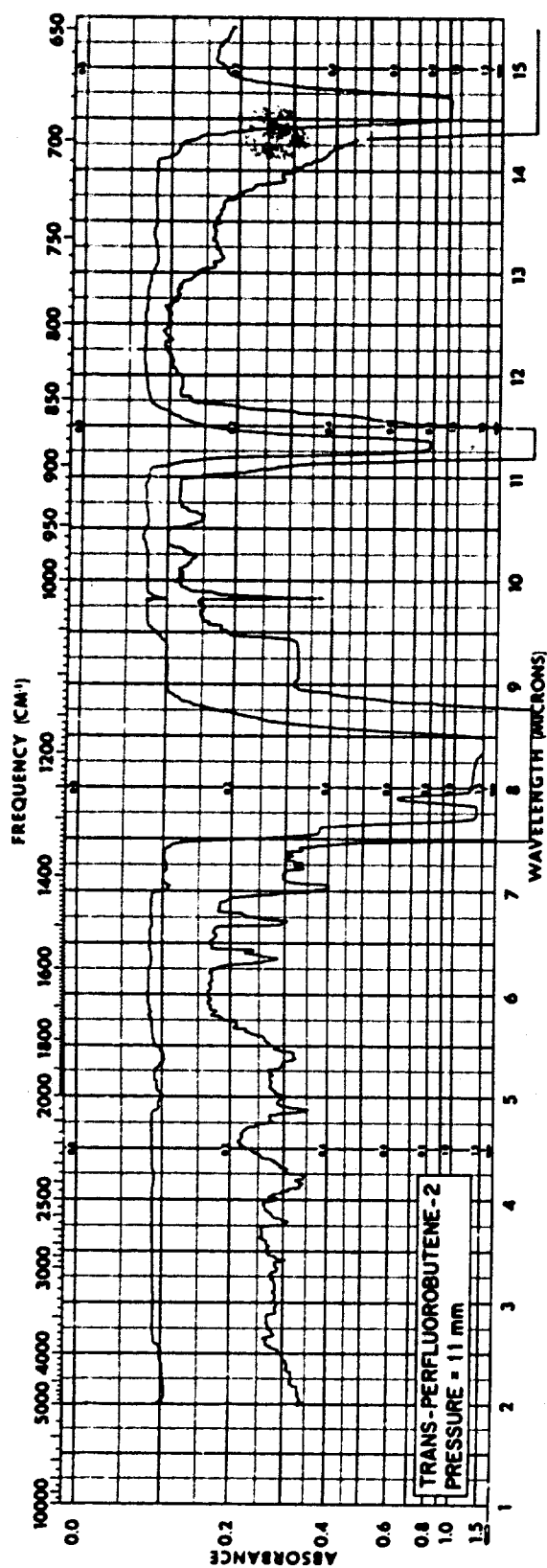


Fig. 1. Infrared spectra. (Continued)

Path length 10 cm. Discontinuity at 9.82μ due to change in optical system. For the curve with more intense absorption, the ordinate has been magnified five times.

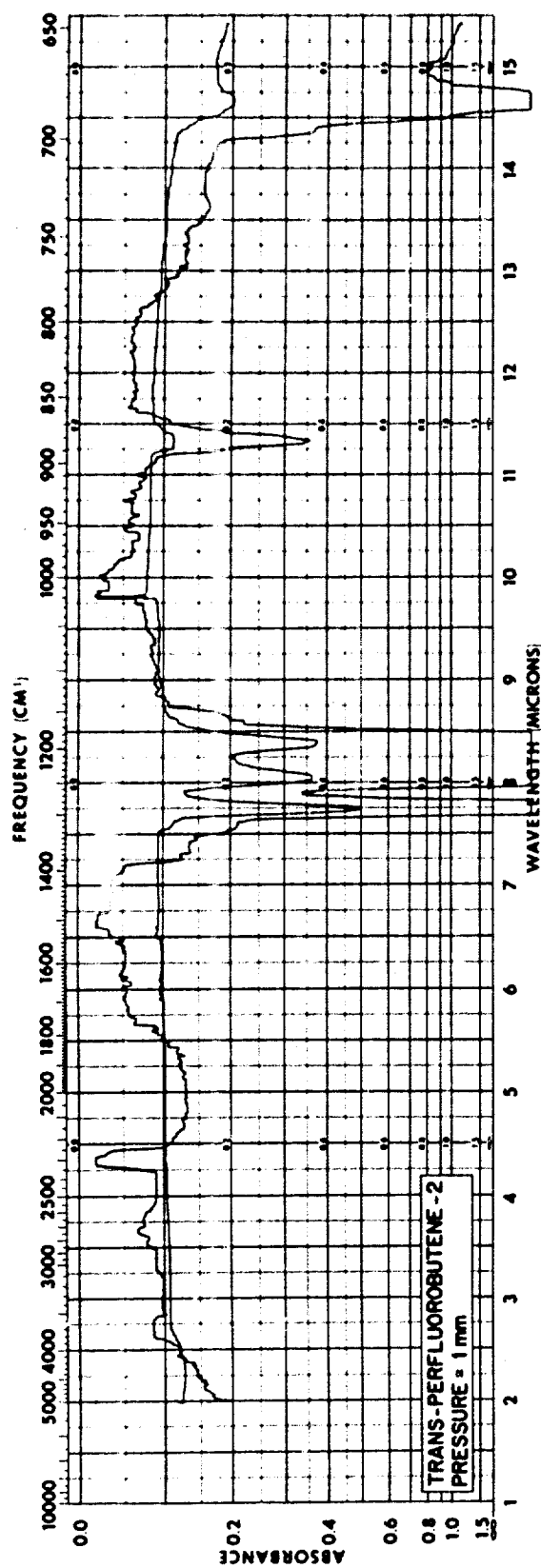


Fig. 1. Infrared spectra. (Continued)

Path length 10 cm. Discontinuity at $9.82\ \mu$ due to change in optical system. For the curve with more intense absorption, the ordinate has been magnified five times.

Table I. Infrared frequencies.

ν , cm^{-1}	Relative intensity	ν , cm^{-1}	Relative intensity
cC_3F_6			
859	s	1172	vw
932	w	1272	vs
978	w	1368	s
1111	w	2532	w
1135	w		
$\text{Cis-C}_4\text{F}_8-2$			
719	vs	1224	vs
726	sh	1245	vs
760	m	1287	m
766	m	1350	vs
905	vw	1389	m
952	vs	1481	vw
956	sh	1524	vw
1064	sh	1562	w
1111	vs	1686	sh
1156	sh	1724	s
1166	sh	1779	m
1193	vs		

Table I. Infrared frequencies. (Cont nued)

ν , cm^{-1}	Relative intensity	ν , cm^{-1}	Relative intensity
Trans-C ₄ F ₈ -2			
682	vs	1387	m
696	sh	1424	m
712	m	1451	vw
730	vw	1499	m
760	m	1527	w
875	sh	1560	w
878	sh	1582	m
882	s	1751	w
890	sh	1848	m
945	m	1953	w
982	m	2000	w
1070-1105	m	2053	m
1149	sh	2105	w
1163	sh	2353	m
1193	vs	2512	w
1242	vs	2652	w
1292	vs	2932	w
1321	sh	3003	w

s = strong, m = medium, w = weak, v = very, sh = shoulder

Table II. Vibrations of cis- and trans- C_4F_8 -2.

Description	Trans symmetry	Cis symmetry
In-plane motions		
C=C stretch	Ag	A ₁
C-F stretch	Ag	A ₁
C-C stretch	Ag	A ₁
CF ₃ symmetric stretch	Ag	A ₁
CF ₃ asymmetric stretch	Ag	A ₁
C-F bend	Ag	A ₁
C-C bend	Ag	A ₁
CF ₃ symmetric bend	A _g	A ₁
CF ₃ asymmetric bend	Ag	A ₁
CF ₃ coupling wag	Ag	A ₁
C-F stretch	Bu	B ₁
C-C stretch	Bu	B ₁
CF ₃ symmetric stretch	Bu	B ₁
CF ₃ asymmetric stretch	Bu	B ₁
C-F bend	Bu	B ₁
C-C bend	Bu	B ₁
CF ₃ symmetric bend	Bu	B ₁
CF ₃ asymmetric bend	Bu	B ₁
CF ₃ coupling wag	Bu	B ₁

Table II. Vibrations of cis- and trans-C₄F₈-2. (Continued)

Description	Trans symmetry	Cis symmetry
Out-of-plane motions		
CF ₃ asymmetric stretch	Au	A ₂
Skeletal bend	Au	A ₂
Skeletal bend	Au	A ₂
CF ₃ asymmetric bend	Au	A ₂
CF ₃ coupling wag	Au	A ₂
CF ₃ asymmetric stretch	Bg	B ₂
Skeletal bend	Bg	B ₂
CF ₃ asymmetric bend	Bg	B ₂
CF ₃ coupling wag	Bg	B ₂

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